occur at −90.1° (82.2 mole per cent. SO_2) and −6.8° (14.3 mole per cent. SO_2). The broadness of the maximum in the melting point curve indicates considerable dissociation of the compound $C_6H_5(CH_3)_2N:SO_2$ at its melting point. This is confirmed by the fact that the compound prepared in petroleum ether smells strongly of sulfur dioxide. However, the compound is reasonably stable over short periods of time because the values obtained for the system $C_6H_5(CH_3)_2N:SO_2-NC_6H_5(CH_3)_2$ check fairly well the corresponding ones obtained for the system $C_6H_5(CH_3)_2N-SO_2$.

The data of Table II may be used to calculate the apparent molecular weight of the addition compound in dimethylaniline at several concentrations. The values for the apparent molecular weight indicate some association at the lowest concentration and increasing amount with each increase in concentration. This point is being investigated further.

Summary

1. The temperature–concentration diagram for the system $C_6H_5(CH_3)_2N-SO_2$ has been determined.

2. The compound dimethylaniline–sulfur dioxide, $C_6H_5(CH_3)_2N:SO_2$, has been identified and isolated and its congruent melting point determined.

3. Cryoscopic molecular weight measurements for $C_6H_5(CH_3)_2N:SO_2$ dissolved in dimethylaniline indicate association of the solute. The degree of association increases with increasing concentration.

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The Viscosity of Sulfur[1]

BY RAYMOND F. BACON AND ROCCO FANELLI

The viscosity of sulfur has long been known to vary in an exceptional manner with temperature. In spite of its unusual irregularity the literature contains but two attempts to measure it. In both papers the published data are far from agreement.

Rotinjanz[1a] by a capillary method measured the viscosity of sulfur throughout its entire liquid range up to its boiling point. He found that the rate of heating varied the values. With heating rates of 0.27 to 1° per minute the sulfur attained a maximum viscosity at 187° of 52,000 relative to water at 17°. Greater heating rates gave lower values for the maximum viscosity and shifted it to higher temperatures. Preheating the sulfur had a profound effect. The higher the sulfur was preheated when the determination was made with falling temperature, the lower was the maximum viscosity and the higher the temperature at which it occurred. Admixture of iodine and ammonia with the sulfur greatly reduced the viscosity values.

Twelve years later Farr and Macleod[2] using a system of rotating cylinders for measuring the viscosity, published data which differed greatly from those given by Rotinjanz. These authors went to much greater lengths to purify their sulfur and experienced great difficulty in obtaining concordant results. Their maximum value for purified gas-free sulfur occurred at about 200° and was 215 poises. Their maximum for purified sulfur (not gas free) after prolonged exposure to air may have a value as high as 800 poises at about 190°.

Rotinjanz assumed that the temperature of his air-bath was the same as that of the sulfur in the capillary tube and that sulfur crystallized from carbon disulfide was pure. Kellas[3] states that the sulfur used in this work was of doubtful purity. Farr and Macleod state that their carefully purified sulfur had a greenish color. This fact indicates that their sulfur was not completely purified in spite of their efforts to make it so.

The wide discrepancy in the published results and the well-founded suspicion that the sulfur used in both cases was impure seemed to warrant further work on the purification of sulfur and its viscosity.

Experimental Methods

The method employed for measuring viscosity above 160° was to impress a definite vacuum on a capillary tube

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(1) Original manuscript received March 7, 1942.

(1a) L. Rotinjanz, *Z. physik. Chem.*, **62**, 609 (1908).

(2) C. Farr and D. B. Macleod, *Proc. Roy. Soc.* (London), (a) **97**, 80 (1920). In a later paper *ibid.*, **118A**, 534 (1928) these authors admitted that their original sulfur preparation was impure. They stated that the impurity was mercury vapor from the pump. In our work several thermometers were accidentally broken in the sulfur. The presence of mercury did not bring about low viscosity values.

(3) A. M. Kellas, *J. Chem. Soc.*, **113**, 903 (1918).

immersed in the sulfur and to note the time required for the sulfur column to rise a measured distance in the capillary. In such a system the viscosity is readily calculated by using Poiseuille's equation; the instrument and procedure were calibrated against a Bureau of Standards oil sample P1 with a given value of 656.1 poises at 30°.

For the temperature range 118 to 160° the modified Ostwald viscometer was used in a paraffin-bath.

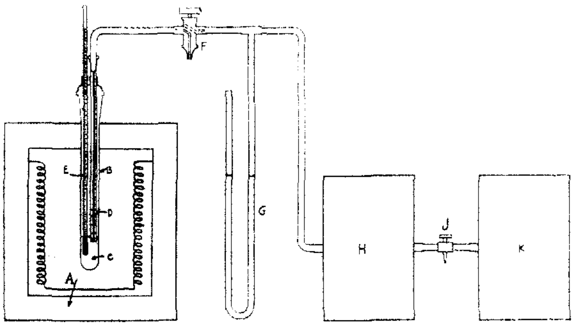

Fig. 1.—Apparatus.

The setup employed is shown in Fig. 1. A is an electric air-bath heavily lagged by glass wool. The coiled heating element (800 watts) is symmetrically suspended from the cylindrical transite shell, 7 inches in diameter and 12 inches long, and also along the bottom. A Fenwall thermal regulator (not shown) enables one to vary the temperature up to 315°. The voltage was controlled by means of a variable transformer. This setup gave good temperature control. B is a Pyrex glass tube 24 cm. long and 3 cm. inside diameter with 24/45 upper joint with corresponding two-holed cap to accommodate a thermometer and the capillary tube. C is 25–30 g. of liquid sulfur at atmospheric pressure. D is a capillary tube, over-all length 34 cm. with a bore of about 1.25 mm., and ringed one centimeter apart at the lower end. The upper end terminates in a 12/30 joint. E is a 360° thermometer reading directly in half degrees and calibrated by the Bureau of Standards. F is a two-way stopcock. G is an open water manometer. H is a surge tank of approximately 10 liters capacity. J is a variable leak and K is a direct motor-driven air pump. 1725 r. p. m. with a capacity of 3.5 c. f. m.

The transite shell contained two Pyrex windows set one behind the other. Both windows when not in use were covered with small thick cork sections which could be removed so as to expose a minimum amount of window surface. During a determination one rear cork section was replaced by a 6-watt mazda lamp with an aluminum foil reflector. This was sufficient to illuminate the interior of the air-bath.

In order to cover the wide range of viscosities encountered in this work a pipet (shown in Fig. 1a) was used. For viscosities above 25 poises the time of rise was measured within the capillary tube. For viscosities below 25 poises the liquid was allowed to rise into the tube graduated in milliliters.

Because of the disturbing effect produced by minute amounts of organic matter in sulfur it was necessary to use all ground joints dry. This in turn required a modification in the usual procedure for such a setup. The method employed was to keep the pump going continuously after setting a definite vacuum by adjusting the leak J. The manometer settled down to a steady state, fluctuating about 1 millimeter during the determination. Stopcock F which was set so that the pressure in the capillary is atmospheric is now turned in order to impress the measured vacuum on the capillary. The time required for the sulfur column to pass through a definite length of the capillary is noted by means of an electric stop watch reading directly to one-tenth of a second. A reading telescope was used to view the passage of the sulfur surface through the measured distance. That this procedure can give good concordance is shown by the values obtained using the Bureau of Standards oil; the average deviation from the mean of six determinations being about 2 parts per thousand.

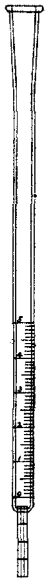

Fig. 1a.

Unlike previous workers the temperature of the sulfur was directly measured by immersion with a glass mercurial thermometer reading in half degrees. This instrument was calibrated by the Bureau of Standards and all necessary corrections were applied to each reading. The temperature of the sulfur was read before and after each determination. It usually remained constant. When it varied it did so by not more than 0.2° in which case the average was taken. The thermometer was also used as the stirrer. At the end of the time period the stopcock F was turned so that the pressure in the capillary would be that of the atmosphere. The column of sulfur slowly drained from the capillary leaving the wall completely free of any liquid sulfur film. Determinations were made about one hour apart. This period permitted complete drainage of the capillary and reheating to the next temperature.

Purification of Sulfur.—The difficulties experienced by Farr and Macleod in obtaining concordant results in spite of their extended efforts to purify the sulfur indicates that some impurity is present which has a marked effect on the viscosity. This impurity is either difficult to remove by the purification methods employed or minute amounts of it greatly modify the viscosity. The source of this impurity is the organic matter which is always found associated with sulfur. The complete removal of this organic matter with its sulfur reaction products is difficult.

The simple method employed for purification of the sulfur used, the tests for the presence of organic matter, the possible impurities in sulfur and the evidence supporting the removal of the organic matter by prolonged boiling of the sulfur in the presence of magnesium oxide are given in detail in a previous paper.[4] The properties of such purified sulfur are different in many respects from those previously reported in the literature.

Viscosity of Sulfur.—The purified sulfur was stored at 125° in the presence of a small amount of magnesium oxide (1%) and was used to obtain the data with rising temperature, pictured in Fig. 3, after the following treatment: no. 97, sulfur as purified—no further treatment, data shown by X; no. 96, sulfur kept in vacuum for thirteen hours, p = 1 mm., data shown by ●; no. 98, sulfur dis-

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(4) R. F. Bacon and R. Fanelli, *Ind. Eng. Chem.*, **34**, 1043 (1942).

tilled—middle portion of distillate kept in vacuum for thirteen hours, p = 1 mm., t = 140°, data shown by ⊙; no. 100, as in 98 except magnesium oxide added to distillate then filtered and filtrate kept in vacuum for twelve hours, P = 1 mm., t = 140°, data shown by ⊗; no. 99, sulfur prepared by hydrogen sulfide–sulfur dioxide reaction in gas phase, then when melted treated with magnesium oxide and filtered, filtrate boiled in presence of magnesium oxide, etc., as in original preparation except for very short period of time. The filtered sulfur was kept in vacuum for thirteen hours, P = 1 mm., t = 140°, data shown by △. All of the data obtained in the above experiments regardless of the varying treatment of the purified sulfur fall upon the same curve. This fact in itself is indicative of the high state of purity that can be obtained by this simple method.

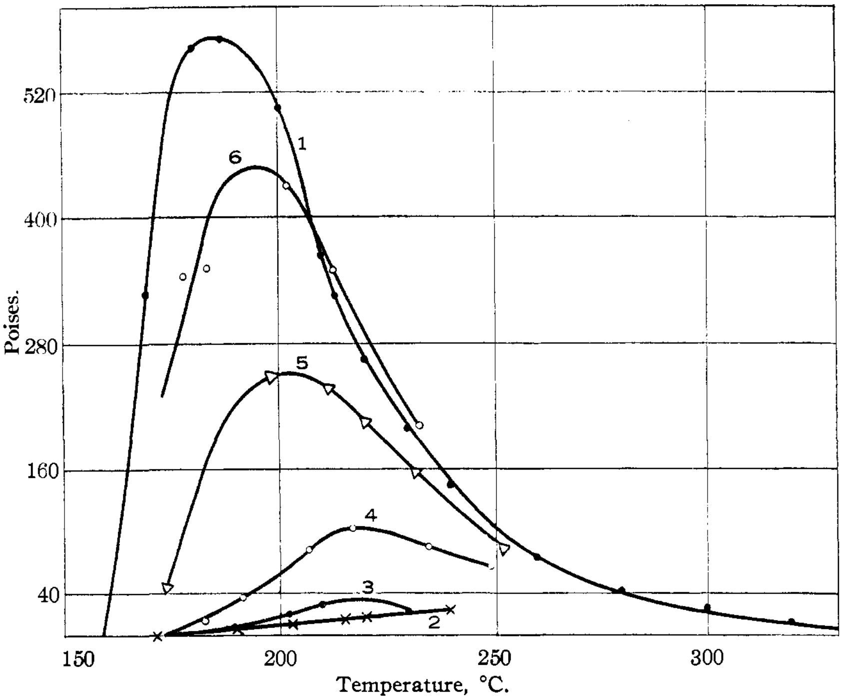

Fig. 2.

The broken curve located by the arrow points is the cooling curve for run no. 100. It falls slightly below the heating curve and is almost identical with it. In all runs with pure sulfur where cooling values were determined this was found to be the case. This is also a mark of purity. The slight lowering of the viscosity curve on cooling is very probably due to the experimental method rather than to some difference in the cooling sulfur. In Rotinjanz' work the cooling curves were far below the heating curves thus indicating that the sulfur used by him was impure.

The maximum viscosity occurs at 186–188°. Ten determinations using the purified mine sulfur and the hydrogen sulfide–sulfur dioxide sulfur gave the following maximum values: 933, 936, 933, 928, 945, 931, 938, 925 and 930. The average value is 932 poises, with an average deviation of about four parts per thousand.

The viscosity of the sulfur purified as described is independent of the rate of heating and its previous heat treatment. This confirms Farr and Macleod's observation in their second paper. Viscosity values for the range up to 160° are pictured in Fig. 3a. The values shown by dots were determined by the modified Ostwald viscometer standardized by a glycerol–water mixture of known value. The crosses are Farr and Macleod's values for this range. They are slightly higher and were obtained by a non-capillary method. This curve shows that in this range the viscosity drops to a minimum at about 157° and then begins to rise. Between 159 and 160° the rise is comparatively sharp.

Effect of Foreign Substances: Organic Matter, SO_2 and H_2SO_4, H_2S, H_2S_x, NH_3 and Amines, Halogens

Effect of Organic Matter.—The profound effect of the presence of organic matter in sulfur on the viscosity is not readily evident until after the sulfur has been heated to a temperature of about 200° and above. A sample of sulfur containing a very small amount of organic matter which has not been previously heated above 180° will give a viscosity curve with rising temperature, similar to curve 1, Fig. 2. This curve is drawn through Rotinjanz' data converted to absolute units. The effect of preheating sulfur containing organic matter is very striking. A sample of sulfur containing 0.038% oil and 0.05% sulfuric acid was raised in a period of one hour from 125 to 260° and kept at this temperature for thirty minutes. The viscosity on cooling is given by curve 2X Fig. 2 and is essentially a straight line. After reaching the low point of 170° the viscosities were redetermined with rising temperature. These values are shown by curve 3. The curve is higher than 2 and shows a well-defined maximum. The sulfur was cooled down to and kept at 160° for fourteen hours and viscosities again determined with rising temperature. The values are shown by curve 4. This cooling and reheating process was twice again repeated and the data are successively pictured by curves 5 and 6 for rising temperature.

This series of experiments is quite revealing. Heating the sulfur at 260° brings about the formation of some reaction product between the sulfur and organic matter which has a tremendous modifying effect on the viscosity. Prolonged heating of this sulfur sample results in higher and higher viscosity curves each with a well-defined maximum which shifts after each run to a lower temperature and which finally approaches that given by a non-preheated impure sample. This behavior indicates that the prolonged heating either slowly destroys or volatilizes the viscosity-modifying substance and that even the presence of minute amounts of it may have a great effect upon some of the properties of sulfur.

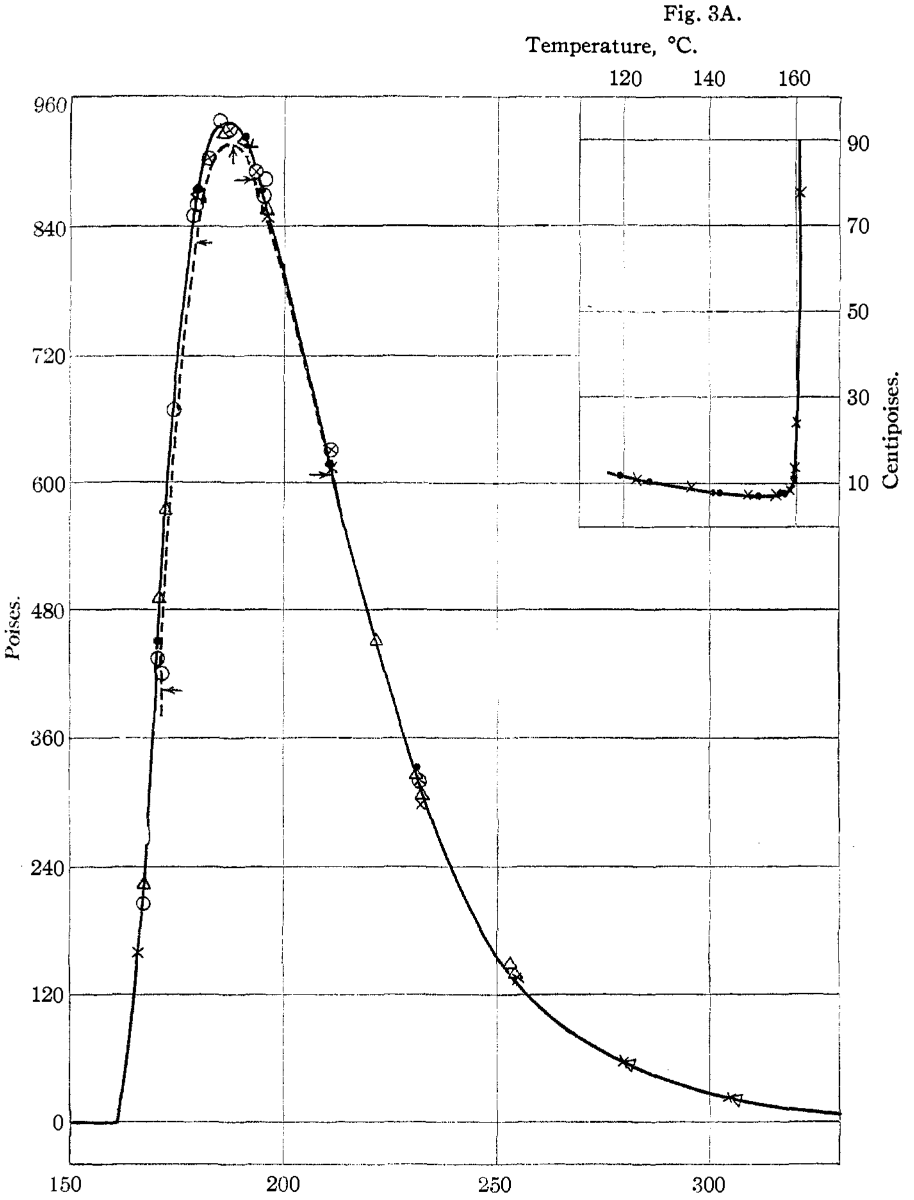

Fig. 3.

These results explain why Rotinjanz obtained lower viscosity curves with falling temperature, and also the dependence of his values on the rate of heating and the previous heat treatment of the sulfur. The higher he heated his sulfur the lower was his viscosity curve on cooling. They also explain why Farr and Macleod obtained higher viscosity values the longer the sulfur was kept liquid and their statement that the maximum value for purified sulfur not gas free after prolonged exposure to air may have a value as high as 800 poises at about 190°. The long heating removed the viscosity modifying component in the sulfur, thus giving a purer sulfur.

Effect of Sulfur Dioxide and Sulfuric Acid.—Sulfur dioxide appears to have no effect on the viscosity of pure sulfur. A pure sample at 136° treated with sulfur dioxide for twenty hours and five hundred and fifty hours gave the same viscosity values as the untreated portion. This confirms Farr and Macleod's observation that passing sulfur dioxide into sulfur even to saturation has only a comparatively slight effect on the viscosity. Sulfuric acid (0.05 cc. of concd. acid to 25 g. of sulfur) had no effect on the viscosity.

Effect of Hydrogen Sulfide.—The effect of hydrogen sulfide seems to have been overlooked by previous investigators. This is surprising in view of the fact that sulfur-containing organic matter when heated evolves hydrogen sulfide and leaves a product which gives very low viscosity values when run with increasing temperature (see Fig. 2).

The curves in Figure 4 show the effect of hydrogen sulfide on the viscosity of sulfur. Curve 1 is a reference curve for untreated sulfur. Curve 2 pictures the values given by the same sulfur sample after it had been treated at 140° with hydrogen sulfide gas for one hundred hours. Both curves 1 and 2 are plotted in arbitrary units and are only approximately correct. The dissolved hydrogen sulfide is not visibly liberated when the determination is thus made with rising temperature. Comparison of the two curves shows that hydrogen sulfide either directly or indirectly lowers the viscosity of sulfur. The sulfur remaining after the determination of the data for curve 2 was cooled down to 140° and treated overnight with hydrogen sulfide in order to replace at least in part what was lost during the viscosity determinations. Viscosities given by this sample are shown by curve 3. The sample was again cooled to 140° and treated with hydrogen sulfide overnight. The viscosities redetermined with rising temperature are pictured by curve 4. Heating the sulfur containing the dissolved hydrogen sulfide through the 180–210° temperature range produces a profound change in the sulfur. The viscosities are now considerably lower than curves 1 and 2. It is significant that sulfur containing organic matter must be heated through this temperature range before it will give low viscosities. This lowering effect is not directly due to the presence of dissolved hydrogen sulfide but to the formation of some reaction product between the sulfur and the hydrogen sulfide. If this is so, then prolonged treatment of sulfur at 140° with hydrogen sulfide should form a greater amount of this reaction product than was formed in the sulfur giving curve 2. Curve 5, which was obtained by treating sulfur at 140° for four hundred hours with hydrogen sulfide and then determining viscosities with rising temperatures, indicates that the above statement is probably correct. Curve 6 pictures the redetermined values with rising temperature after cooling to 170°. The curve is higher than no. 5 with a maximum shifted to a lower temperature. This effect is identical with that shown in Fig. 2, thus showing the close similarity between the two methods of treatment.

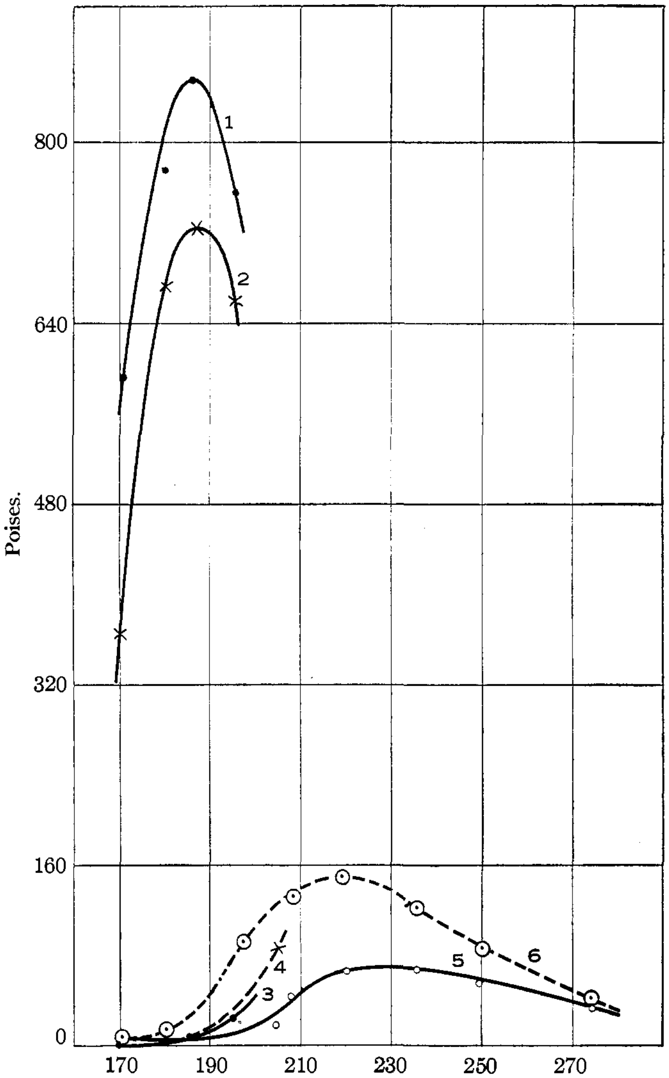

Fig. 4.

If hydrogen sulfide is passed through pure sulfur while slowly raising its temperature from 125 to 190° (one and one-half hours) the sample does not attain the viscous stage. Its viscosity at the end of this period is but 0.90 poise as compared with about 930 for untreated sulfur. Continued treatment for an additional period of one and one-half hours by hydrogen sulfide at this temperature drops the viscosity to about 0.7 poise. Further gassing does not appear to give much lower values at this temperature.

Effect of H_2S_X.—The logical reaction products between hydrogen sulfide and liquid sulfur are the hydrogen persulfides. This class of compounds ranges from H_2S_2 to H_2S_X where X has been reported as high as 10. These compounds are not particularly stable to heat, although the H_2S_2 compound boils with little decomposition at about 75°. Some show rapid decomposition below 100° but their stability is increased by sulfur, dissolved hydrogen sulfide and by certain organic compounds with which they readily form addition products. This stabilizing influence explains why they persist so long in the heated sulfur and why sulfur must be kept at the boiling point for such long periods of time in order to get rid of them completely. In heating sulfur containing oil, the persulfides may form by direct action of the sulfur on the hydrocarbons or by reaction between the nascent hydrogen sulfide and sulfur.

The formation of hydrogen persulfide by reaction of hydrogen sulfide with sulfur offers an explanation for the increased solubility of hydrogen sulfide with rising temperature.

In further confirmation crude hydrogen persulfide was prepared and dried by fused boric acid. Enough persulfide was added to liquid sulfur at 125° to give a solution containing about 5% by weight. This persulfide dissolved without decomposition. Viscosities were determined on this liquid mixture with rising temperature. During the

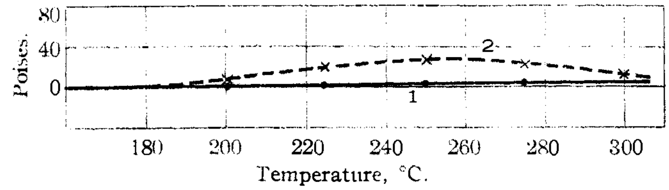

Fig. 5.

heating a large number of gas bubbles formed up to 170° indicating much decomposition or evolution of the persulfide. At the end of this period the amount of persulfide present must have been but a minute portion of the original amount. The viscosity curve given by this mixture is shown in Fig. 5 by curve 1. It is obvious that a small amount of this crude persulfide is extremely effective in reducing the viscosity of sulfur. At the end of this determination the sulfur was cooled down to and kept at 132° for about fourteen hours. Redetermined viscosity values on this sample with rising temperature are shown by curve 2. Here again the heat treatment slowly raises the viscosity values and shifts the maximum viscosity to lower temperatures.

It is therefore concluded from these facts that the hydrogen persulfides are responsible for the low viscosity values given by a preheated sulfur containing organic matter and that the effect of hydrogen sulfide on pure sulfur is to form and stabilize these compounds. Thiophene and other organic sulfides do not reduce the viscosity of sulfur before preheating. The term "preheating" as used in this paper means heating the sample at about 180° and above and then cooling to below 160° before making viscosity determinations.

Effect of Ammonia and Amines.—The effect of ammonia gas on sulfur according to Rotinjanz is to markedly reduce its viscosity. His ammoniated sulfur gave a maximum of 19,000 centipoises as compared with 52,000 for untreated sulfur.

In Fig. 6 are shown the results obtained with rising temperature, using pure sulfur treated with ammonia gas at 140°. Curve 1 shows values for untreated sulfur, curves 2, 3, and 4 for sulfur treated with ammonia for twenty-three, forty and six hundred hours, respectively. These curves show that ammonia does drop the viscosity, but the drop is not nearly so great as reported. In this series of curves prolonged treatment shifts the maximum viscosity to higher temperatures. In all cases where an impurity is present or added which reduces the viscosity, the maximum is shifted to higher temperatures. The greater the concentration of the impurity the higher is the temperature of maximum viscosity.

The lowering effect produced by ammonia is probably due to the formation of minute amounts of hydrogen persulfide and hydrogen sulfide by reaction of the ammonia with sulfur. There is sufficient evidence in the literature to support this view.[5] If pure sulfur is gassed at 190° by ammonia for forty hours the maximum viscosity attains a value of about 600 poises. This indicates that the formation of the hydrogen sulfides by action of ammonia is a slow reaction.

It might be mentioned here that very small amounts of straight chain amines, cycloamines and other compounds with reactive amino groups are very effective in reducing the viscosity of sulfur. This is due to the easy formation of hydrogen persulfide, its addition products and hydrogen sulfide.

Effect of Halogens.—A number of factors favor the use of sulfur as a heat transfer liquid. It is cheap, stable and has a low vapor pressure throughout almost its entire liquid range. Its greatest drawback is its high viscosity temperature curve. Any stable substance which reduces this viscosity is therefore of interest.

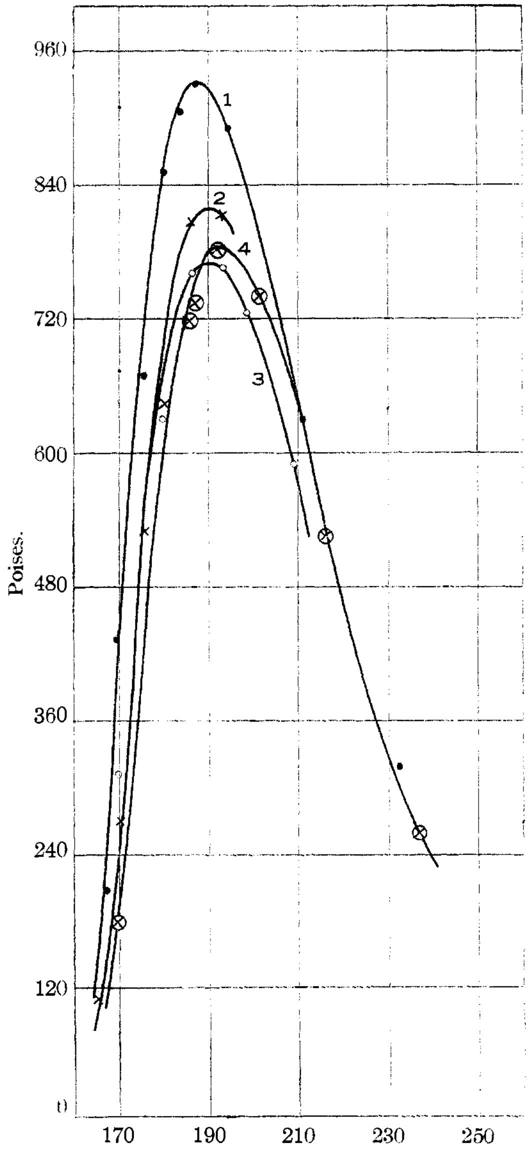

Fig. 6.

Organic matter and hydrogen persulfides are not the only substances which reduce the viscosity of sulfur. Rotinjanz has shown how effective iodine can be in concentrations of

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(5) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, p. 217.

(6) L. Hammick and M. J. Zvegintzov, *J. Chem. Soc.*, 273 (1930).

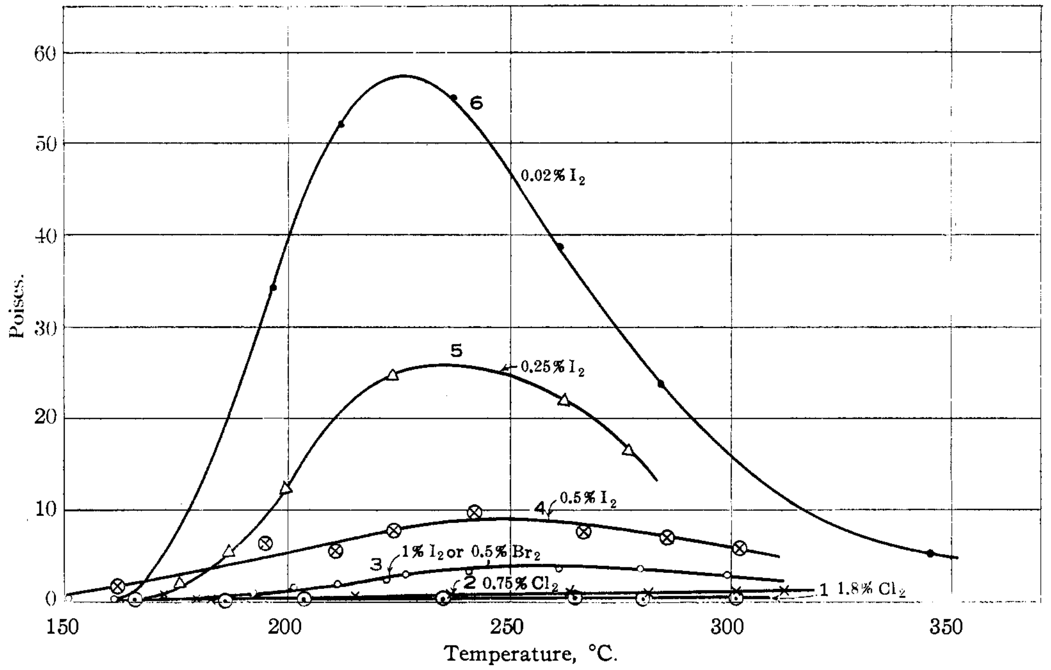

Fig. 7.

0.02% and 0.77%. Hammick and Zvegintzov[6] noticed that sulfur sealed in a glass tube with 2% sulfur chloride remained a mobile liquid when heated to 180°. The effect of other members of the halogen family seems not to have been tried.

Experiments were made using sulfur plus chlorine, bromine and iodine mixtures. The chlorine was added to the sulfur in the form of sulfur chloride, the iodine and bromine in the elemental state. The viscosity temperature curves are shown in Fig. 7.

Curves 1 and 2 show the effectiveness of chlorine in the form of sulfur chloride in reducing the viscosity. The 1% iodine and the 0.5% bromine curves practically coincide and are higher than the 0.75% chlorine curve. Curves 4, 5, and 6 show the effect of diminishing iodine concentrations. Curve 6 is drawn through Rotinjanz' data. Here again increasing concentrations show a shift of maximum viscosity to higher temperatures. The position of the curves indicates that the order of decreasing effectiveness for the halogens is chlorine, bromine, and iodine. Fluorine would probably head the group.

The persistency of the effect produced by the halogens was determined by maintaining the mixtures at 190–200°, and from time to time determining the viscosity at 200°.

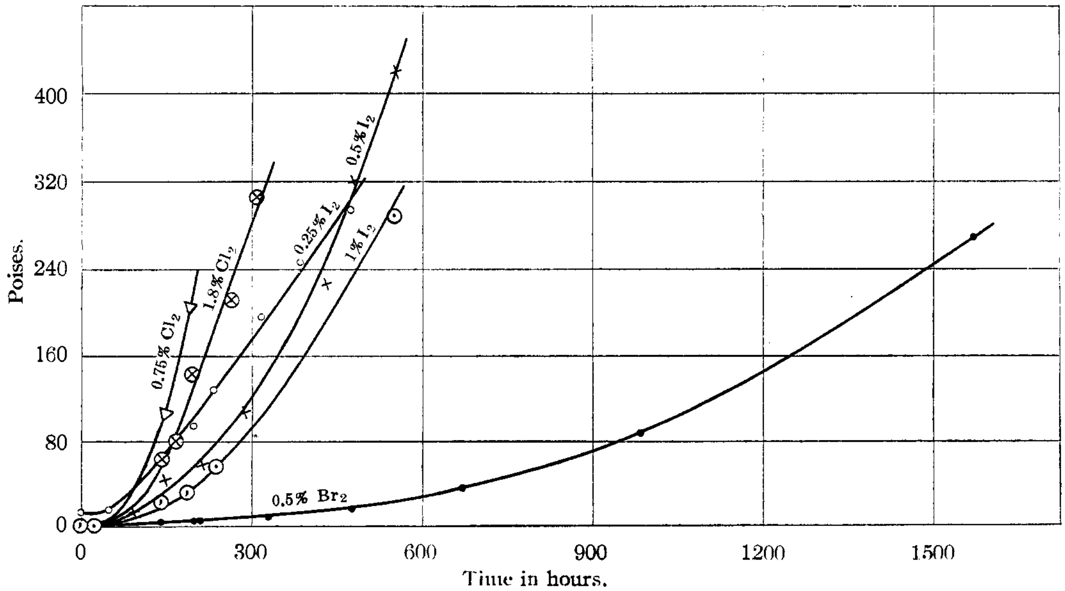

Fig. 8.

The system was kept open so that volatile matter could escape. The data obtained are plotted in Fig. 8. While chlorine is most effective in reducing the viscosity of sulfur its volatility in the form of sulfur chloride is greatest. Iodine is better than chlorine whereas bromine is by far the best. These results are consistent with the following boiling points: sulfur chloride, 138°; iodine, 184°; sulfur bromide, 58° at 0.22 mm. pressure.

All of these substances in a closed system will maintain a low viscosity in sulfur over a long period of time. A number of metals now marketed will successfully resist attack by these mixtures.

The data used in plotting the curves in Fig. 3 are as follows (all viscosity values are in poises).

FIG. 3.

t, °C.	μ
No. 96	
170	450
180.3	871
186.5	931
191.6	926
195.7	869
211.3	624
231.1	326
No. 99	
166.1	225
170.1	491
172.4	579
180.5	866
186.9	925
191.6	920
196	857
213.5	572
221.7	450
231.5	316
252.9	146
253.6	139
280.1	55
305.8	23

t, °C.	μ
No. 97	
164.8	160
170.1	436
180.5	857
186.7	933
192.9	918
196.2	855
211.7	613
232	302
253.5	136
279.6	53
280	52
306.1	21
No. 100	
165.5	206
169.7	432
175	667
180.2	850
183.2	905
187.2	931
195.5	889
211	628
232.1	320

t, °C.	μ
No. 98	
170	418
180.8	861
186.7	881
196.3	869
No. 100 Cooling	
211.5	610
194	884
188	915
180.3	824

FIG. 3a

118.7	0.1146
118.8	.1145
125.7	.1031
132.7	.0884
140.7	.0767
141.4	.0756
142.5	.0744
151.6	.0662
157.3	.0672
159.2	.116

Discussion

Several explanations have been advanced to account for the unusual viscosity–temperature relationship of sulfur. Smith and Holmes[7] showed that liquid sulfur is an equilibrium mixture of two modifications, one, $S\lambda$, soluble in carbon disulfide, the other $S\mu$, insoluble in this solvent. With rise in temperature $S\mu$ increases at the expense of $S\lambda$. At 160° the rise is sharp. Above this point the concentration of $S\mu$ steadily rises to a maximum above 35% at the boiling point. During normal cooling $S\mu$ readily reverts to $S\lambda$. Smith believed that the rise in viscosity was due to the presence of $S\mu$ in the liquid.

A number of objections may be cited against this explanation. (1) The viscosity attains a maximum value at about 187° and then sharply drops to a comparatively very low value of about 20 poises at 310°, whereas the $S\mu$ concentration steadily rises to a maximum value at the boiling point. (2) The viscosity of a 2% solution of iodine in sulfur shows a maximum value of less than 2 poises, whereas according to Smith and Carson[8] in this solution the concentration of $S\mu$ is almost double that of untreated sulfur throughout the entire liquid range. (3) According to Smith and Holmes, ammonia inhibits altogether the transformation of soluble to insoluble sulfur, yet pure sulfur gassed with ammonia still gives a very high viscosity curve (see Fig. 6). Farr and Macleod[2] tried to show a relationship between $S\mu$ and the viscosity, but their results were conflicting and inconclusive. They believed that the high viscosity was due to the presence of sulfuric acid and dissolved gases.

Hammick and Zvegintzov[6] state that $S\mu$ as such is not present in liquid sulfur but makes its appearance when the liquid solidifies.

Aten's[9] description of another modification, $S\pi$, present in the liquid can hardly be advanced as an explanation of the high viscosity, as its concentration is constant at about 5% throughout the entire liquid range.

The belief that the rise in viscosity with temperature is due to the polymerization of sulfur into long chains is well founded. The indirect[3] and direct evidence supporting this view seems to be conclusive. The tendency of sulfur to form long chains is shown by the easy formation of elastic or chilled sulfur. Trillat and Forestier[10] have shown that elastic sulfur gives a fiber-diagram. Meyer and Go[11] and Meyer[12] deduce that the sulfur atoms are present in long chains arranged parallel to the direction of stretching. Strong[13] has determined the stress-strain curves for elastic sulfur and found that they are very similar to those given by raw rubber. So impressed was he by the similarity in properties of raw rubber and elastic sulfur that he stated: "If a means of vulcanizing and stabilizing plastic sulfur could be devised it might prove a worthy substitute for rub-

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(7) **A. Smith and W. B. Holmes**, *Z. physik. Chem.*, V. **42**, 469 (1903) and V, **54**, 257 (1906).

(8) A. Smith and C. M. Carson, *ibid.*, **77**, 661 (1911); THIS JOURNAL, **29**, 499 (1907).

(9) A. H. Aten, *Z. physik. Chem.*, **81**, 257 (1912); **83**, 442 (1913); **86**, 1 (1914); **88**, 321 (1914).

(10) J. J. Trillat and H. Forestier, *Bull. Soc. Chim.*, **51**, 249 (1932); see also N. S. Gingrich, *J. Chem. Phys.*, **8**, 29 (1940).

(11) K. H. Meyer and Y. Go, *Helv. Chim. Acta*, **17**, 1081 (1934).

(12) K. H. Meyer, *Trans. Faraday Soc.*, **32**, 148 (1936).

(13) J. D. Strong, *J. phys. chem.*, **32**, 1225 (1928); see also K. Sakurada and H. Erbing, *Kolloid. Z.*, **72**, 129 (1935).

ber since it costs but a few cents per pound." The close resemblance in physical properties indicates the same type of molecular structure.

Warren and Burwell[14] by X-ray analysis show that the sulfur molecule in the orthorhombic and monoclinic forms is an eight numbered puckered ring, and that not too far above the melting point it is still S_8. Their explanation of the high viscosity is that the ring ruptures with rising temperature, forming long chains which tangle with each other. Ewell and Eyring[15] by calculation from viscosity data confirm the presence of S_8 molecules in the liquid below 160°.

These facts would seem to indicate that in liquid sulfur the equilibrium $S_8 \rightleftarrows S_n$ (chain) prevails. At low temperatures near the melting point the S_8 molecule predominates and as the temperature rises to 160° these molecules rupture. The viscosity curve between 80–160° shows a gradual drop to a minimum value at about 157° (see Fig. 3a and ref. 2) thus indicating a simplification in the molecular composition of the liquid preparatory to the sharp rise in viscosity. Above 160° the chains become longer and longer, reaching the maximum length at about 187°. Beyond this point the falling viscosities indicate that increasing the temperature rapidly shortens the chains until at the boiling point numerous short chains predominate in the liquid. The mechanism is not as simple as indicated. The large sulfur molecule may contain branch chains either straight or ring or both, and may itself be a huge ring rather than a long straight chain, although the idea of long straight chains is accepted as the most likely structure. Contrary to previous work, we have shown that with pure sulfur there is a practical coincidence of the viscosity cooling curve with the heating curve regardless of the rate of heating and cooling and of the previous heat treatment of the sulfur. This indicates that the equilibrium is essentially independent of the direction of heating and that polymerization and depolymerization are rapid and of the same degree at any one temperature. If the viscosity were dependent upon heating rates one would expect the greatest variation in the maximum value. However, it was found that raising the temperature to 187° at different rates gave the same maximum value.

If the high viscosity is due to the polymerization of sulfur into long chains, then the reduction of the viscosity by the halogens, hydrogen sulfide and hydrogen persulfides must be due to a reaction which shortens the chains or breaks rings. This division of the chain is believed to be brought about by the halogen atoms taking the terminal positions of the segments, thus for iodine we would have I–S–S–S · · · S–S–I. In the same way hydrogen sulfide and hydrogen persulfides shorten the chains with hydrogen as the terminal atoms of the segments. Such a mechanism would explain why these substances persist so tenaciously in the liquid sulfur even when the mixture is kept far above their boiling points.

Length of the Sulfur Chain.—The length of the sulfur chain is of primary interest because of its structural similarity to that of raw rubber. In view of the elemental nature of sulfur this analogy in structure is of great importance in that it provides a simple substance for fundamental study in chain formation. Such a study might throw some light upon the underlying causes of elasticity and plasticity.

The number of sulfur atoms in the chain is not known, although it is believed to be very high. Trillat and Forestier[10] by X-ray analysis of elastic sulfur claim to have demonstrated the presence of an elementary cell consisting of 112 atoms. Ewell and Eyring[15] believe that long chains move in segments made up of a definite number of atoms. For sulfur chains they calculate from viscosity data that the moving segment contains 36 atoms, and indicate that the concept of tangled chains to explain the rise in viscosity postulated by Warren and Burwell[14] is unnecessary if the unit of flow is made up of at least 36 atoms. Kauzmann and Eyring[16] using Flory's equation[17] calculate the weight average length of the sulfur chains (above 200°) as 12,000 atoms. Flory's constants are based on carbon, therefore this value of 12,000 atoms is dependent upon whether these constants also hold for sulfur.

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Summary

1. Viscosity values are given for pure sulfur which are believed to be closer to the true values than those in the literature.

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[14] B. E. Warren and J. T. Burwell, *J. Chem. Phys.*, **3**, 6 (1935).

[15] R. H. Ewell and H. Eyring, *ibid.*, **5**, 726 (1937).

[16] W. Kauzmann and H. Eyring, THIS JOURNAL, **62**, 3113 (1940).

[17] P. J. Flory, *ibid.*, **62**, 1057 (1940).

2. The viscosity of pure sulfur is independent of the rate of heating and cooling and of the previous heat treatment of the sulfur. The viscosity cooling curve practically coincides with the heating curve.

3. It has been shown that the low viscosities given by preheated sulfur containing organic matter are due to the formation of hydrogen persulfides and that preheating has no effect on the values for pure sulfur.

4. Curves showing the lowering effect of hydrogen persulfide on the viscosity of sulfur are given.

5. The effect of gases on the viscosity of sulfur is described. Hydrogen sulfide through reaction with sulfur to form persulfides greatly reduces the viscosity of sulfur. The lowering effect by ammonia gas is due to minute formation of hydrogen sulfide and persulfides by reaction with the sulfur.

6. The presence of minute amounts of hydrogen persulfides and hydrogen sulfide in sulfur profoundly affects its viscosity and probably other physical properties. It is believed that traces of these substances are responsible for much of the lack of concordance in the physical data of sulfur.

7. The effect of the halogens on lowering the viscosity of sulfur is shown in detail. Because of the persistence of this effect, sulfur so treated can be used as a heat transfer medium.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Properties of Liquid Sulfur

BY RICHARD E. POWELL AND HENRY EYRING

Introduction.—It is well known that when molten sulfur is heated above about 160°, the mobile liquid changes into an extremely viscous liquid. The low-temperature liquid (S_λ) has been shown to consist of 8-membered puckered rings,[1] and there is considerable evidence that the high-temperature liquid (S_μ) is made up of long sulfur chains. The two forms are supposed to be in dynamic equilibrium. The recent investigation by Bacon and Fanelli[2] of the viscosity of specially purified sulfur has shown, in addition to other important results, that the equilibrium is rapidly and completely reversible. It is the purpose of this paper to formulate a quantitative theory for the equilibria and for the viscosity of molten sulfur, based upon the current picture of the behavior of long-chain polymers.

We shall assume that the equilibria in molten sulfur are given by the reaction

$$\frac{x}{8}\, S_{8\,(\text{ring})} \rightleftharpoons S_{x\,(\text{chain})} \quad 0 < x < \infty \qquad (1)$$

The polysulfur chains are not all of the same length, but there is a distribution of chain lengths. Among the experimental evidences for this model of polysulfur are the following which support the existence of long chains.

(a) S_μ, produced by chilling viscous sulfur or from the vapor above viscous sulfur, is insoluble in carbon disulfide.[3,4]

(b) The extremely high viscosity of S_μ is characteristic of long-chain polymers.[5,6,2]

(c) Chilled S_μ gives elastic threads, which may be stretched 800-fold, and give fiber-patterns upon X-ray analysis.[7,8,9,10]

(d) Liquid S_λ (120–150°) shows "structure-viscosity."[11]

(e) The Eötvös relation, applied to the surface tension of molten sulfur, indicates that S_λ is about S_6 while S_μ is about S_{18}.[12] (At the present time, this is to be interpreted as a segment length and not as the length of the molecule[13]).

The following are evidences for the existence of short chains:

(f) The molecular weight of sulfur in the vapor state indicates that the molecule is S_8 only at low

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(1) B. E. Warren and J. T. Burwell, *J. Chem. Phys.*, **3**, 6 (1935).

(2) R. Bacon and R. Fanelli, THIS JOURNAL, **65**, 639 (1943).

(3) A. Smith, *et al.*, *Z. physik. Chem.*, **42**, 469 (1903); **52**, 602 (1905); **54**, 257 (1906); **57**, 685 (1907); **61**, 200, 209 (1908); **77**, 661 (1911).

(4) D. L. Hammick, W. Cousins and E. Langford, *J. Chem. Soc.*, 797 (1928).

(5) L. Rotinjanz, *Z. physik. Chem.*, **63**, 609 (1908).

(6) C. C. Farr and D. B. McLeod, *Proc. Roy. Soc. London*, **A97**, 80 (1920).

(7) J. Trillat and H. Forestier, *Bull. soc. chim.*, **51**, 248 (1932).

(8) J. D. Strong, *J. Phys. Chem.*, **32**, 1225 (1928).

(9) K. Sakurada and H. Erbring, *Kolloid. Z.*, **72**, 129 (1935).

(10) K. H. Meyer and Y. Go, *Helv. Chim. Acta*, **17**, 1081 (1934); K. H. Meyer, *Trans. Faraday Soc.*, **32**, 148 (1936).

(11) W. Ostwald and H. Malss, *Kolloid. Z.*, **63**, 305 (1933).

(12) A. M. Kellas, *J. Chem. Soc.*, **113**, 903 (1918).

(13) W. Kauzmann and H. Eyring, THIS JOURNAL, **62**, 3113 (1940).